



UNITED STATES PATENT AND TRADEMARK OFFICE

I, Susan ANTHONY BA, ACIS,
Director of RWS Group plc, of Europa House, Marsham Way, Gerrards Cross,
Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That the translator responsible for the attached translation is well acquainted with the German and English languages.
3. That the attached is, to the best of RWS Group plc knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in Germany on 16. 3. 2001 under the number DE 101 12 651 A1 and the official certificate attached hereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

For and on behalf of RWS Group plc

The 5th day of August 2004

19 **FEDERAL REPUBLIC
OF GERMANY**

[crest]

**GERMAN PATENT
OFFICE**

12 **Offenlegungsschrift**
11 **DE 101 12 651 A 1**

51 Int. Cl.7:
C 01 B 33/187
A 61 K 47/04
B 01 J 21/08

21 File reference 101 12 651.4
22 Date of application 16. 3. 2001
43 Date laid open 19. 9. 2002

DE 101 12 651 A 1

73 Patent proprietor:
Degussa AG, 40474 Düsseldorf, DE

72 Inventors:

Uhrlandt, Stefan, Dipl.-Chem. Dr., 53859
Niederkassel, DE; Schmoll, Ralf, Dipl.-Chem.
Dr., 53125 Bonn, DE; Drexel, Claus-Peter,
Dipl.-Chem., Dr., 63263 Neu-Isenburg, DE

The following details are taken from the documents submitted by the applicant

- ⑤4 Inhomogene Kieselsäuren als Trägermaterial
⑤7 Die Erfindung betrifft Kieselsäuren mit homogener
Struktur bzw. Aufbau, Verfahren zu deren Herstellung und
deren Verwendung als Trägermaterial für Vitamine oder
Cholinchlorid.

- ⑤4 Inhomogeneous silicas as carrier material

The invention relates to silicas having an
inhomogeneous structure or composition, to processes
for preparing them, and to their use as carrier
material for vitamins or choline chloride.

DE 101 12 651 A 1

Description

The invention relates to silicas having an inhomogeneous structure or composition, to processes
5 for preparing them, and to their use as carrier material.

Readily dispersible silicas are prepared, for example, in accordance with EP 0 901 986 or EP 0 647 591 by
10 precipitating waterglass with sulfuric acid, followed by drying. The dried products are subsequently ground and/or granulated.

By means of mechanical granulation, any silica can be
15 prepared in dust-free form; however, this additional process step generally brings about a deterioration in the dispersibility.

In another process, silicas are prepared, likewise by acid precipitation, but are dried by spraying with hot
20 air and at the same time are shaped into beads, which are easily destroyed. Thus EP 018 866 describes the preparation of spray-dried silica having an average particle diameter of more than 80 μm , the particles
25 being solid and possessing a homogeneous structure.

Spray-dried silicas in accordance with EP 0 018 866 are particularly suitable as carrier material since they are dust-free and possess a high sorbency. Dust freedom
30 is an important criterion for the processing of the silica, since simple processing of the silicas without corresponding suction exhaust units is of great economic importance. Besides freedom from dust, the specific surface areas (BET, CTAB) and the oil
35 absorption capacity (DBP) are important for the carrier material utility.

In contrast to mechanical granulation, spray drying cannot be used to prepare all silicas in dust-free form.

- 5 One type of silica generally does not meet all of the required criteria. A mixture of two or more types of silica is frequently preparable only with an excessive dust content.
- 10 It would be desirable to prepare a silica which at one and the same time covers broad ranges of physicochemical data such as BET or CTAB surface area, and has good absorbency and a low dust content. As already stated, this cannot be achieved for all silicas
- 15 by means of spray drying or granulation.

It has surprisingly been found that silica that has an inhomogeneous composition is readily adjustable to meet the requirements that are called for and yet has good

20 absorbency and a low fines content.

The present invention accordingly provides silicas comprising at least two silica fractions which differ by at least 10% in at least one value for BET surface

25 area, CTAB surface area, and DBP absorption.

The silicas of the invention are therefore particularly suitable as carrier material for active substances such as vitamins and choline chloride, for example.

30 The structure of the silicas, comprising at least two silica fractions, results in an inhomogeneity of the silica, which is reflected at the same time in good absorbency and a low fines content and comprises the

35 required physicochemical data.

Silicas of the invention possess a fines content of not more than 10% with a particle diameter of less than or equal to 63 μm (Alpine sieve residue).

- 5 A similar concept is pursued in EP 0 942 029. There, compositions are described which comprises a precipitated silica in two different aggregate sizes. The different aggregate sizes are employed for the ready dispersibility of the silica in a rubber blend.
- 10 The different silica fractions of the present invention are not described in these publications; moreover, in the present case a different aggregate size of the silica fractions is of secondary importance - what are important are the differences in the physicochemical
- 15 data. The use of silicas as carrier materials is not described in EP 0 942 029.

For the purpose of the present invention, a silica fraction refers to different grades of silicas which, owing to different preparation processes or process variants, have a difference of 10% in at least one of the abovementioned physicochemical data. Such a difference exists preferably for two, with particular preference three, of these parameters.

- 25 The differences in the abovementioned parameters may be obtained by means of different processes of preparing the silica fractions. Accordingly, all, one or more of the silica fractions may be precipitated silicas and/or
- 30 pyrogenic silicas. In the case of precipitated silicas in particular it is possible to obtain different silica fractions by means of different precipitation processes. Silicas of the invention may also be prepared from fractions of precipitated and pyrogenic
- 35 silicas.

For precipitated silicas as carrier material, a variety of precipitation methods are known and may be read

about, for example, in EP 0 937 755 or EP 0 643 015. In the examples, illustratively, two precipitated silicas from different preparation processes have been processed to give the inhomogeneous silica of the invention. It is also possible to combine hydrophobicized silica fractions with untreated silica fractions to give the silica of the invention.

The silica fractions may be precipitated silicas or pyrogenic silicas, and the fractions may be mixed at different steps in the process that are normally carried out in the preparation of silicas.

When using fractions of precipitated silicas, mixing may take place following the precipitation of silicate with an acid (generally waterglass, i.e., sodium silicate, with sulfuric acid) by mixing together the precipitation suspensions or the filtercakes obtained following filtration of the suspensions, and also liquefied (resuspended) filtercakes. It is also possible to add ready-prepared, dried or hydrophobicized silica fractions, as solids, to the suspensions or to the filtercakes.

The mixtures obtained in this way may need to be filtered and dried in a customary manner. Examples of drying processes are spray drying, jet tower, rack drier, rotary tube drier, and spin flash drier processes.

Drying may be followed by a final grinding and/or granulation step.

It is also possible to mix the silica fractions in the dry state. This may be followed by resuspension, with the above drying steps, and/or by grinding/granulation.

Silicas of the invention may have the following physicochemical data:

	BET surface area	100 - 900 m ² /g, especially 150 - 600 m ² /g
5	CTAB surface area	100 - 500 m ² /g, especially 150 - 400 m ² /g
	DBP absorption	150 - 350 g/100 g

These physicochemical data relate to the silica according to the invention per se, and not to the silica fractions.

In the manner described, the physicochemical data of the silica fractions must differ by at least 10%, preferably by at least 15%, with particular preference by at least 20%.

The physicochemical data are determined by the following methods:

20	BET surface area	Areometer, from Ströhlein, to ISO 5794/Annex D
	CTAB surface area	at pH 9 by the method of Jay, Janzen and Kraus in Rubber Chemistry and Technology 44 (1971) 1287
25	DBP number	ASTM D 2414-88

The invention additionally provides a process for preparing silicas comprising at least two silica fractions, in which at least two silica fractions which differ by at least 10% in at one least one value for BET surface area, CTAB surface area and DBP absorption are mixed with one another.

The proportion of the respective fractions in the suspension or of the silica should in each case be between 5 and 95% by weight, based on the dry silica.

The silica is preferably obtained, by spray drying, for example, in a particle form having an average diameter of more than 80 μm , in particular more than 100 μm , with particular preference more than 200 μm . The
5 suspension may be spray-dried in accordance, for example, with US 4 097 771.

The silicas of the invention may therefore be used as carrier material, especially for adsorbing liquid
10 active substances.

The silicas of the invention can be used in particular as carriers for vitamins (A, B, C, E), where appropriate in acetate form, proteins, enzymes or
15 choline chloride.

Furthermore, the silica may be used as a support for catalytically active substances.

20 Moreover, the silicas of the invention may be used in all areas of application in which silicas are customarily used, such as in battery separators, antiblocking agents, flatting agents and paints, paper coating slips or defoamers, for example.

25 The silica of the invention or the silica fractions may be modified in a known manner, i.e., hydrophobicized, with silanes, with silicone oil and/or with organosilanes.

30 Procedure for determining the Alpine sieve residue

To determine the sieve residue, the silica or silicate sample is passed through a 500 μm sieve in order to destroy any devolatilization agglomerates that may be
35 present. Then 10 g of the sieved sample are placed on the air jet sieve, with a 63 μm sieve mesh, and are sieved at 200 mm water column underpressure. Particles of silica or silicate which settle on the sieve cover

of the apparatus are knocked off by careful tapping on the button of the sieve cover. The sieving operation generally lasts 5 minutes. It is at an end when the residue remains constant, generally evident from the free-flowing appearance. Sieving is then continued for one more minute in order to be on the safe side.

If any agglomerates form, the sieving operation is briefly interrupted and the agglomerates are broken down under gentle pressure using a brush. After sieving, the sieve residue is carefully knocked from the air jet sieve and reweighed. The sieve residue is expressed in percent, always in conjunction with the mesh size of the sieve.

15

Calculation

$$\% \text{ of sieve residue} = \frac{A \cdot 100}{E}$$

A = final weight in g

20 E = initial weight in g

Apparatus

Alpine air jet sieve, laboratory type S 200

Vacuum cleaner or fan

25 Air jet sieve with sieve mesh 63 μm to DIN 4188

Precision balance

The examples which follow are intended to illustrate the invention without restricting its scope.

30

Two silica fractions were prepared, A in accordance with US 1 043 282 or DE 24 47 013 and B in accordance with DE 31 44 299, and the suspensions obtained from the precipitations were reacted further in the manner described below.

35

Example 1

The precipitation suspensions of the silica fractions A and B were mixed in a 50:50 ratio. This was done by mixing 80 kg of the precipitated silica A (solids content approximately 46 g/l) with 80 kg of the precipitated silica B (solids content approximately 64 g/l) in a stirred vessel. The resulting mixture was filtered and the filtercake was liquefied with a small amount of acid and sprayed in a jet tower drier. The analytical data are compiled in Table 1.

Example 2

The precipitation suspensions of the silica fractions A and B were mixed in a 70:30 ratio. This was done by mixing 112 kg of the precipitated silica A (solids content approximately 46 g/l) with 48 kg of the precipitated silica B (solids content approximately 64 g/l) in a stirred vessel. The resulting mixture was filtered and the filtercake was liquefied with a small amount of acid and sprayed in a jet tower drier. The analytical data are compiled in Table 1.

Example 3

The precipitation suspensions of the silica fractions A and B were mixed in a 30:70 ratio. This was done by mixing 43.8 kg of the precipitated silica A (solids content approximately 46 g/l) with 102.2 kg of the precipitated silica B (solids content approximately 64 g/l) in a stirred vessel. The resulting mixture was filtered and the filtercake was liquefied with a small amount of acid and sprayed in a jet tower drier. The analytical data are compiled in Table 1.

Example 4

A mixture of the dried silica fractions (50:50) was prepared.

Table 1:

Comparison of the analytical data from Examples 1-3 and of silica fractions A and B:

		Silica fraction A	Silica fraction B	Differences of fractions A:B in %	Example 1	Example 2	Example 3	Example 4
Loss on ignition, DIN	%	5.0	5.0		3.7	2.7	3.4	10.1
Water content	%	5.0	4.5	10	5.3	5.3	5.5	5.6
pH reading		6.5	6.0	7.6	6.2	6.4	6.4	6.6
Conductivity	μS	800	700	12.5	600	740	610	750
BET surface area	m^2/g	195	195	00	354	403	284	302
CTAB surface area	m^2/g	175	350	50	271	302	232	256
DBP absorption	$\text{g}/100 \text{ g}$	263	335	21.5	281	287	265	296
Tapped density	g/l	280	180	36.7	200	185	217	222
Alpine sieve residue 63 μm	%	80	> = 20		99	91	99	52
Alpine sieve residue 180 μm	%	> = 4	1		82	18	87	4.5
Alpine sieve residue 250 μm	%	n.d.	n.d.		75	1.1	48	

What is claimed is

1. A silica comprising at least two silica fractions,
5 **wherein** said at least two silica fractions differ
by at least 10% in at least one value for BET
surface area, CTAB surface area and DBP
absorption.
- 10 2. The silica as claimed in claim 1, which is in the
form of particles having an average diameter of
more than 80 μm .
- 15 3. The silica as claimed in either of claims 1 and 2,
which has the following physicochemical data:
BET surface area 100 - 900 m^2/g ,
CTAB surface area 100 - 500 m^2/g ,
DBP absorption 150 - 350 g/100 g.
- 20 4. The silica as claimed in any of claims 1 to 3,
wherein the respective proportion of one silica
fraction in the silica is between 5 and 95% by
weight.
- 25 5. The silica as claimed in any of claims 1 to 4,
which is hydrophobicized.
- 30 6. The silica as claimed in any of claims 1 to 5,
wherein at least one silica fraction is
hydrophobicized.
- 35 7. The silica as claimed in any of claims 1 to 6,
wherein one or more silica fractions comprise a
precipitated silica.
8. The silica as claimed in any of claims 1 to 7,
wherein the silica fractions are prepared by

precipitating silicate with an acid and the resulting precipitation suspensions are mixed.

- 5 9. The silica as claimed in any of claims 1 to 7,
 wherein the silica fractions are prepared by
 precipitating silicate with an acid, the
 precipitation suspension is filtered, and the
 resulting filtercakes are mixed.
- 10 10. The silica as claimed in any of claims 1 to 7,
 wherein the silica fractions are prepared by
 precipitating silicate with an acid, the
 filtercakes or ready-dried silica are liquefied,
 and the resulting suspensions are mixed.
- 15 11. The silica as claimed in any of claims 1 to 6,
 wherein one or more silica fractions comprise a
 pyrogenic silica.
- 20 12. The silica as claimed in any of claims 1 to 7 and
 11, wherein the silica fractions are mixed in the
 dried state.
- 25 13. A process for preparing silicas comprising at
 least two silica fractions, which comprises mixing
 with one another at least two silica fractions
 which differ by at least 10% in at least one value
 for BET surface area, CTAB surface area and DBP
 absorption.
- 30 14. The process as claimed in claim 13, wherein the
 silica is in the form of particles having an
 average diameter of more than 80 μm .
- 35 15. The process as claimed in either of claims 13 and
 14, wherein the silica has the following
 physicochemical data:

BET surface area 100 - 900 m²/g,
CTAB surface area 100 - 500 m²/g,
DBP absorption 150 - 350 g/100 g.

- 5 16. The process as claimed in any of claims 13 to 15,
 wherein the respective proportion of one silica
 fraction in the silica is between 5 and 95% by
 weight.
- 10 17. The process as claimed in any of claims 13 to 16,
 wherein the silica is hydrophobicized.
18. The process as claimed in any of claims 13 to 16,
 wherein at least one silica fraction is
15 hydrophobicized.
19. The process as claimed in any of claims 13 to 18,
 wherein one or more silica fractions comprise a
 precipitated silica.
- 20 20. The process as claimed in any of claims 13 to 19,
 wherein the silica fractions are prepared by
 precipitating silicate with an acid and the
 resulting precipitation suspensions are mixed.
- 25 21. The process as claimed in any of claims 13 to 19,
 wherein the silica fractions are prepared by
 precipitating silicate with an acid, the
 precipitation suspension is filtered, and the
30 resulting filtercakes are mixed.
22. The process as claimed in any of claims 13 to 19,
 wherein the silica fractions are prepared by
 precipitating silicate with an acid, the
35 filtercakes or ready-dried silica are liquefied,
 and the resulting suspensions are mixed.

23. The process as claimed in any of claims 13 to 18, wherein one or more silica fractions comprise a pyrogenic silica.
- 5 24. The process as claimed in any of claims 13 to 19 and 23, wherein the silica fractions are mixed in the dried state.
- 10 25. The use of the silica as claimed in any of claims 1 to 12 as carrier or support material.
- 15 26. The use of the silica as claimed in any of claims 1 to 12 as carrier material for vitamins, vitamin acetates, choline chloride, proteins or enzymes.
27. The use of the silica as claimed in claim 26 as support material for catalytically active substances.